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Note

Low-temperature thermal reactions between SO_2 and H_2O_2 and their relevance to the jovian icy satellites

Mark J. Loeffler *, Reggie L. Hudson

NASA Goddard Space Flight Center, Astrochemistry Branch, Code 691, Greenbelt, MD 20771, USA

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ABSTRACT

Here we present first results on a non-radiolytic, thermally-driven reaction sequence in solid $H_2O + SO_2 + H_2O_2$ mixtures at 50–130 K, which produces sulfate (SO_4^{2-}), and has an activation energy of 53 kJ/mole. We suspect that these results may explain some of the observations related to the presence and distribution of H_2O_2 across Europa's surface as well as the lack of H_2O_2 on Ganymede and Callisto.

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1. Introduction

The radiation-driven chemistry of surface and near-surface ices of Europa has been studied by several research groups in recent years. In contrast, thermally-driven reactions in outer Solar System ices have remained relatively unexplored. In this note we report new laboratory experiments demonstrating that a straightforward sequence of hydrolysis, protonation, and redox chemistry can convert SO_2 into SO_4^{2-} (sulfate) at the temperatures of Europa's surface and in the presence of H_2O_2 (hydrogen peroxide), a well-known radiation product of H_2O–ice. These reactions suggest that sub-surface SO_4^{2-} formation will occur in the absence of the direct reach of jovian magnetospheric radiation.

Laboratory studies of H_2O–ice, one of the more abundant substances on cold surfaces in outer space, have shown that radiation can cause both amorphization of crystalline H_2O–ice (Hudson and Moore, 1995; Strazzulla et al., 1992) and the production of new molecules, such as H_2O_2, H_2, and O_2. Of these three species, H_2O_2 (hydrogen peroxide) formation has been observed *in situ* by laboratory infrared (IR) spectroscopy in H_2O–ice irradiated at temperatures relevant to extraterrestrial surfaces (Loeffler et al., 2006a; Moore and Hudson, 2000; Zheng et al., 2006). Although all of these prior studies showed that the H_2O_2 abundance is relatively low in irradiated H_2O–ice, the H_2O_2 absorption at 3.5 μm is well-separated from the stronger OH stretching vibrations of water, making it an attractive candidate for observation on planetary surfaces if both H_2O–ice and radiation are present.

Given the many extraterrestrial objects with surficial H_2O–ice exposed to radiation, one might expect to find H_2O_2 on a great number of icy bodies. However, H_2O_2 has been detected unequivocally only on Europa (Carlson et al., 1999), with IR spectra of Ganymede and Callisto failing to show the 3.5-μm peroxide band. Interestingly, ultraviolet spectra of Ganymede do show O_3 (Noll et al., 1996), a reliable indicator of radiation processing of H_2O–ice containing O_2. Differences exist among surface environments of Europa, Ganymede, and Callisto, such as concerning radiation flux, average surface temperature, and composition, but so far none of these factors readily explains why Europa would be the only place where H_2O_2 is present.

In recent years we have used IR spectroscopy to investigate the solid-phase radiation chemistry of $H_2O + SO_2$ ices (Moore et al., 2007), solid sulfuric acid, and sulfuric acid hydrates (Loeffler and Hudson, 2012; Loeffler et al., 2011), all at temperatures relevant to the icy jovian satellites. With $H_2O + SO_2$ ices, it was observed that radiation readily produces SO_4^{2-} (sulfate ion), presumably by the oxidizing action of radiolytically-generated H_2O_2. This assumption has been tested in the present paper by studying IR spectra of *unirradiated* $H_2O + SO_2 + H_2O_2$ ices as they are warmed. We have observed that even at relatively low temperatures, H_2O_2 and SO_2 react thermally in the presence of H_2O–ice. The main products of the reaction have been identified and the reaction's rate has been measured at 110–122 K, temperatures found on the jovian icy satellites mentioned above.

2. Experimental methods

Experiments were performed with a cryostat ($T_{min} \sim 10$ K) operating in a stainless steel high-vacuum chamber ($P \sim 1 \times 10^{-7}$ Torr). Ice films were prepared by co-deposition of H_2O, H_2O_2, and SO_2 onto a pre-cooled (50–100 K) gold-coated aluminum mirror using three separate pre-calibrated gas lines. Pure H_2O_2 was prepared in a glass manifold, using the technique described previously (Loeffler and Baragiola, 2011). During deposition, the sample's thickness was monitored with interferometry using a diode laser (670 nm). In all experiments the thickness of the resulting $H_2O + SO_2 + H_2O_2$ (80:14:6) ice was 1.3 ± 0.1 μm, assuming indices of refraction at 670 nm are similar to those measured in the visible region, 1.31 for H_2O (Merwin, 1930), 1.4 for H_2O_2 (Giguère, 1943) and 1.36 for SO_2 (Musso et al., 2000), uniform mixing, and an ice density of 0.96 g/cm^3 (0.82 g/cm^3 for H_2O (Westley et al., 1998), 1.6 g/cm^3 for H_2O_2 (Loeffler et al., 2006b) and 1.49 g/cm^3 for SO_2 (Weast, 1983).

Each sample's IR spectrum was recorded before, during, and after warming at 1 K/min to the annealing temperature (110–130 K). Spectra of ices were measured from 7000 to 400 cm^{-1} with a Bruker Vector Fourier Transform infrared spectrometer at 2-cm^{-1} resolution and with 200-scan accumulations. To obtain a spectrum, the reflectance from the ice-coated substrate was ratioed against the reflectance of the bare substrate, taken before ice formation, and then converted to absorbance units.

* Corresponding author.
E-mail address: mark.loeffler@nasa.gov (M.J. Loeffler).

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To quantify the kinetics of the thermal reactions occurring in our samples, we first fit the baseline of the 2850 cm^{-1} overtone band of H_2O_2 with a non-linear curve and then integrated this same H_2O_2 IR feature. We chose to examine H_2O_2 and not SO_2 because the sublimation of pure H_2O_2 is negligible below 130 K, whereas the sublimation of pure SO_2 can become significant above 100 K, the temperature region of interest. We note that when H_2O_2 is dispersed in water the strength of the 2850 cm^{-1} band depends slightly on temperature (Loeffler et al., 2006a). This dependence was confirmed in H_2O–H_2O_2 calibration experiments and we made use of it in our calculations; the strength of the H_2O_2 band in question drops linearly by about 20% between 50 and 130 K.

3. Results

Fig. 1 shows the IR spectrum of an $H_2O + SO_2 + H_2O_2$ (80:14:6) ice after deposition at 50 K, during warming to 118 K, and while held at 118 K. At 50 K, each of the three molecules of the sample is easily identified in this spectral region: H_2O_2 (2845 cm^{-1}), H_2O (1655 cm^{-1}), and SO_2 (1329 and 1151 cm^{-1}). On warming to 118 K, new absorptions, belonging to HSO_3^- (1035 cm^{-1}), SO_4^{2-} (1092 cm^{-1}), and $S_2O_5^{2-}$ (954 cm^{-1}) appeared, as did a broadening on the high-wavenumber side of the H_2O band at 1655 cm^{-1}, indicating H_3O^+ formation. As the sample was annealed at 118 K, the main SO_4^{2-} band continued to increase, other weaker bands of SO_4^{2-} (606 cm^{-1} and 980 cm^{-1}) appeared, and the H_2O_2 and SO_2 bands decreased significantly. Fig. 2 shows the H_2O_2 abundance in the sample as a function of time (50 K; $t = 0$) for annealing temperatures of 110, 118, and 130 K. In all cases the H_2O_2 abundance began to decrease around 100 K and continued to fall as the sample was annealed. For the samples held at 110 and 118 K, the H_2O_2 abundance dropped by a factor of two and a factor of eight, respectively, after 1200 min, while only ~20 min were needed at 130 K for the H_2O_2 abundance to drop below the noise level. Blank experiments with H_2O–H_2O_2 showed that over these same time periods there was no H_2O_2 loss, as expected from the negligible sublimation rate of H_2O_2 at 130 K.

The inset of Fig. 2 shows an Arrhenius plot derived from six different annealing temperatures, which together yielded an activation energy of 53 ± 5 kJ/mole. The rate constant, k, was derived from $N = N_o \exp(-kt)$, since we observed that, to a first approximation, the H_2O_2 abundance (N) dropped exponentially with time (t) at each temperature studied. In the higher temperature experiments, the reaction began before we reached the annealing temperature, so in all cases we calculated k by equating it to $\ln(2)/t_{1/2}$, where $t_{1/2}$ is the time at the annealing temperature needed for the H_2O_2 abundance to drop to half of its original value. We note that as the abundance of H_2O_2 has already dropped by a factor of two by the time we warm to ~125 K (see 130 K experiment in Fig. 2), we only used annealing temperatures below 122 K to calculate the activation energy. The error that we give in the activation energy is a combination of the difficulty of fitting the H_2O_2 baseline, the narrow temperature range (12 K) for which we can obtain a value for $t_{1/2}$, and the fact that at the upper temperatures the reactions already have proceeded to some extent by the time the sample attained those temperatures. Future studies will focus on reducing the uncertainty in these measurements by extending the experiments to lower temperatures so that the activation energy can be more-confidently used below 100 K.

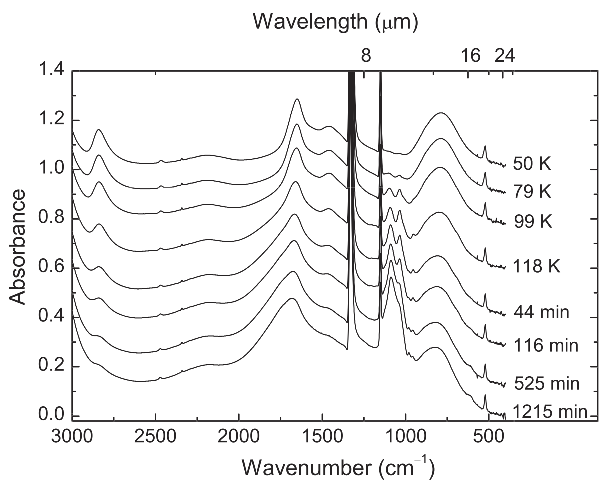

Fig. 1. Evolution of a $H_2O + SO_2 + H_2O_2$ sample (80:14:6) during heating to and annealing at 118 K. The bottom four spectra are labeled by the time elapsed after the sample had reached 118 K.

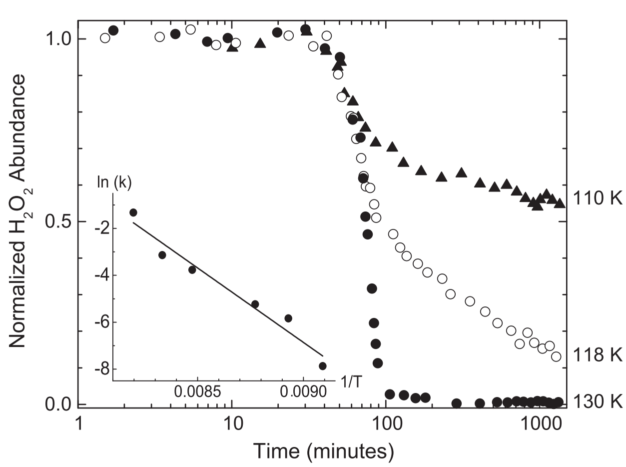

Fig. 2. Evolution of a $H_2O + SO_2 + H_2O_2$ sample (80:14:6) during heating to and isothermal annealing at 110, 118, and 130 K. All samples were deposited at 50 K and warmed at 1 K/min. Inset: Arrhenius plot for the $H_2O + SO_2 + H_2O_2$ reaction. The line's slope yields an activation energy of 53 kJ/mole.

4. Discussion

4.1. Reaction chemistry

Thermal reactions between SO_2 and H_2O_2 have been studied extensively within the atmospheric-chemistry community due to the importance of such chemistry in removing SO_2, in liquid, gas, and solid phases, from Earth's atmosphere. The primary reaction sequence is believed to begin with the formation of bisulfite (HSO_3^-) through (1)

$$H_2O + SO_2 \rightarrow HSO_3^- + H^+ \tag{1}$$

where the H^+ either rapidly or in concerted fashion attaches to a second H_2O molecule to form hydronium:

$$H^+ + H_2O \rightarrow H_3O^+ \tag{2}$$

In our previous studies with $H_2O + SO_2$ ices, we found that these thermal reactions occur in the solid state even at temperatures below 100 K (Loeffler and Hudson, 2010). We now find, in addition, that in the presence of H_2O_2 the bisulfite is oxidized to form the sulfate (SO_4^{2-}) ion (Martin and Damschen, 1981):

$$H_2O_2 + HSO_3^- \rightarrow SO_4^{2-} + H_3O^+ \tag{3}$$

Fig. 1 provides evidence that these same thermally-induced reactions occur in our $H_2O + SO_2 + H_2O_2$ ices. Beginning with the 50-K spectrum and working toward those for higher temperatures, IR absorptions of both HSO_3^- (1035 cm^{-1}) and SO_4^{2-} (1092 cm^{-1}) products can be seen starting at ~80 K during warming. Both bands continued to increase with temperature until the SO_4^{2-} feature was one of the more-prominent remaining IR absorptions. The increase in abundances for the HSO_3^- and SO_4^{2-} ions correlated with the decrease in absorption band areas of reactants SO_2 and H_2O_2 (Fig. 1), supporting the simple reaction sequence already described. Comparing the H_2O_2 loss for our different annealing temperatures, we see that not surprisingly the reaction proceeds the fastest at the highest temperature. However, even at the lower temperatures, the H_2O_2 abundance is still decreasing after the longest times studied (~1200 min), indicating that given enough time all of the H_2O_2 will convert to SO_4^{2-} via reaction (3).

4.2. Icy satellite implications

Infrared spectra of the surface of Europa, Ganymede, and Callisto all contain an absorption at 4.05 μm, which usually is assigned to SO_2 (Hansen and McCord, 2008; Hibbitts et al., 2000; McCord et al., 1998). In contrast, the 3.5-μm band of H_2O_2 has been found only in Europa's spectra (Carlson et al., 1999; Hansen and McCord, 2008). Our experiments show that the abundance of H_2O_2 in these surface ices depends on the presence of SO_2, and that, conversely, sulfur dioxide's abundance will be influenced by the presence of H_2O_2. Given these new laboratory results, we now turn to some of the previous observations of the jovian icy satellites.

On Europa, although both H_2O_2 and SO_2 have been detected they do not appear to be uniformly distributed. Hansen and McCord (2008) determined that the SO_2 infrared feature was present on Europa's trailing hemisphere. This agrees with previous measurements of Europa's ultraviolet reflectance spectrum (Domingue and Lane, 1998; Hendrix et al., 2011; Hendrix and Johnson, 2008; Lane et al., 1981), which showed a strong slope on the moon's trailing side, attributed to SO_2 (0.28 μm band center). It also is consistent with the sulfur implantation rate being an order of magnitude higher on Europa's trailing hemisphere (Johnson et al., 2004).

Interestingly, the more-recent ultraviolet measurements indicate that SO_2 is not only more abundant on the trailing side but that it is actually absent on the leading side, where the majority of the H_2O_2 detections have been made (Carlson et al., 1999). Thus, based on our results it seems plausible that the distribution of SO_2 and H_2O_2 may be a result of excess SO_2 consuming any H_2O_2 produced by radiolysis in the trailing hemisphere and excess H_2O_2 consuming the SO_2 formed by implantation in the leading hemisphere. Finally, we point out that one recent study did detect both H_2O_2 and SO_2 in a spectrum of an ice-rich region on Europa's trailing side (Hansen and McCord, 2008). However, it is possible that these two molecules may be spatially separated, but sufficiently close to lie within the same pixel area of the detector.

On Callisto and Ganymede the 3.5-μm absorption diagnostic of H_2O_2 is absent, which could indicate that surficial SO_2 is widespread or that the H_2O_2 abundance is simply much lower than on Europa (Hendrix et al., 1999; Hendrix and Johnson, 2008). The former possibility is consistent with IR measurements of Ganymede and Callisto (McCord et al., 1998), which showed that each satellite's spectrum contained the 4.05-μm absorption band attributed to SO_2. However, we note that there has been some discussion as to whether another species, such as H_2CO_3 or other carbonates (Johnson et al., 2004), could provide an adequate match for the 4.05-μm feature in Callisto's spectrum, as this band does not seem to be correlated with magnetospheric bombardment (Hibbitts et al., 2000). Also, the most recent ultraviolet measurements show little variation across Callisto's surface (Hendrix and Johnson, 2008).

As the $H_2O + SO_2 + H_2O_2$ reaction we studied occurs quickly at temperatures relevant to these icy satellites ($t_{1/2} \sim 1$ yr at 100 K and $\sim$0.3 h at 120 K), we expect that it plays an important role in the evolution of the jovian icy satellites' surface chemistry and may explain observations of Europa related to the presence and distribution of H_2O_2 as well as the lack of H_2O_2 on Ganymede and Callisto. If other molecules prove to be reactive with H_2O_2 at these or at even lower temperatures, then similar thermal chemistry may explain why H_2O_2 has not been detected on most Solar System icy bodies exposed to radiation. Future laboratory studies will focus on extending the reported measurements to other temperatures and concentrations, identifying and quantifying other thermal reactions that may occur between H_2O_2 and other astrochemically-relevant molecules, and establishing whether the reaction products contain IR absorptions which could be detected by remote sensing. Finally, we note that the reactions we have described are not restricted to the surface of Europa and other worlds. To the extent that vertical transport of radiolytic products occurs (Greenburg, 2010), our reactions (1)–(3) also will take place beneath the IR-sensed layer of Europa, providing a thermally-driven source of SO_4^{2-}.

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